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On the Structural Inhomogeneity in Glass Network. (I)

Vitreous Silica

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Based on the experimental fact that the X-ray pattern of vitreous silica may be interpreted as an assembly of 4 to 8 Si-O rings an idea was advanced which states that SiO_2-network may be resolved into a number of small solid structures, "structure units." Structure units may be classified, and formulated accrding to the apices of the structure, or to the rings contained. There are a good number of possible structure units, but they are not countless.

For each structure unit the hole volume, the volume of void space of the open structure assigned to an unit, may be evaluated from the data of the density.

There is a set of structure units which gives a definite density value although there may be other ones having different bond distances and angles.

In order to show the utility of the conception of structure unit two more properties, the diffusion of gases through vitreous silica and the melting and devitrification, have been interpreted in the light of the structure of the network.

INTRODUCTION

It is generally accepted that glass is a typical homogeneous material. Although it is by no means an easy job to produce the glasses being sufficiently homogeneous to meet the severe specifications, for example, for optical use it is still within our reach.

A glass being perfectly homogeneous in all directions from the macroscopic view point is, however, not homogeneous enough from the microscopic point of view, that is to say, such perfect glass has still the structure which varies from point to point. The randomness, or inhomogeneity of structure may be regarded as the fate which was sealed to the material when it became a glass.

Even in vitreous silica, which is chemically so simple as SiO_2, and even if it were physically perfectly homogeneous without including any defect it is generally accepted as having a random structure. Although this conception of random network has been postulated long before by Zachariasen[1] and supported by X-ray analysis of Warren[2] the lack of long range order in the structure seems to have prohibited the further approach to the detail of such network. In fact, so far as the author knows, there are only two attempts to formulate the random network, one the structon theory of Huggins[3] and the other the vitron theory of Tilton.[4]

In this paper the author is going to present his view of the inhomogeneity of glass structure, and taking vitreous silica as an example, try to formulate

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the "structure unit" which corresponds to the unit cell of crystal, and then try to interpret some properties of glass in terms of the volume and arrangement of structure units.

1. Experimental Backgrounds

The present arguments rest on the results obtained by the investigation of Oberlies and Dietzel[5] who worked out the statistic distribution of the existence of 4-, 5-, 6-, 7-, and 8-Si rings and found that the well known Warren's X-ray pattern may be interpreted satisfactory if we assume the predominance of hexagonal ring in the network, so that the structure of vitreous silica takes after high cristobalite lattice more than it has been assumed. The starting point of the present discussion is the fact that the X-ray pattern may be adequately interpreted if we assume the existence of square to octagonal rings in the network.

2. The Model

It is very convenient, and is often necessary to use solid models for the better understanding of solid structures. In our models an oxygen was represented by a rubber sphere of 27 mm in diameter having a hole through the center in order to thrust pins from both sides. The flexibility of rubber allows us to make the Si-O-Si angles varying from 151°2′ (square ring) to 178°33′ (pentagonal ring), and 180° (hexagonal ring) etc.

For a silicon atom a steel ball of 8 mm diameter with 4 horns making each other the tetrahedral angles of 109°28′ was used in order to represent the strong directional nature of O-Si-O bond. To represent a solid structure two models were constructed, namely, one the ordinary model containing Si and O, and the other the Si-skeleton model in order to study more precisely the relative position of silicon atoms. For this purpose the rubber oxygen balls were replaced by aluminium tubes.

In our model Si and O have the radius of 4 and 13.5 mm, respectively, which give the Si-O distance of 17.5 mm, about 1.3 mm larger than the value of 16.2 mm corresponding to the experimental value. Probably this difference would be the result of the negligence of the overlapping of charge clouds due to the covalent nature of the bonds. As our purpose is to know only the relative position of the atoms as clear as possible, the covalent nature of the bonds has been neglected.

3. The Structure Unit

Although the starting point of our arguments is the fact that the X-ray pattern of vitreous silica may be analyzed by assuming the Si-O network is built from an assembly of Si-O rings, the author would like to stress the fact that the rings are connected to form a number of different solid structures.

From a crystal network we may single out an assembly of small number of atoms, a unit cell, a structure unit having the same symmetry, from the whole crystal. By piling up regularly the unit cells it is possible to construct the whole crystal having the desired crystallographical characteristics.

Needless to say that the lack of the long range regularity in glass structure prohibits us to carry out such an operation. It is not possible to set up any kind of unit cell of a glass network whose assembly represents the whole structure. Admitting all the nature of random network it is still possible to carry out the operation of separating the whole structure into a number of small solid structures each composed of Si-O rings, and containing some void spaces or holes. This may be done by counting all the rings twice except those at the surface.

By this operation we obtain many kinds of small solid structures containing different number of atoms, which may be classified according to the number of apices, the number of atoms composing the rings,.etc. The solid structures as well as their groups may be formulated to give simple formulae which represent, at least to some extent, the geometrical and physical nature of the structure. We shall use the word the *structure unit* to represent such solid structures. Let us explain the difference between a unit cell of a crystal and a structure unit of a glass network by an example :

A unit cell of high cristobalite contains 18 Si, of which 8 Si are shared with 8 cells and 6 with two cells so that it is formulated as $Z=8SiO_2$.

In glass network we generally do not know what structure unit will come to the next. Therefore, instead of taking $Z=8SiO_2$ cell as a unit the author is going to use a solid structure made up from four 6 Si-rings, which is the same as the exclusion of 8Si atoms from the corner of an ordinary unit cell.

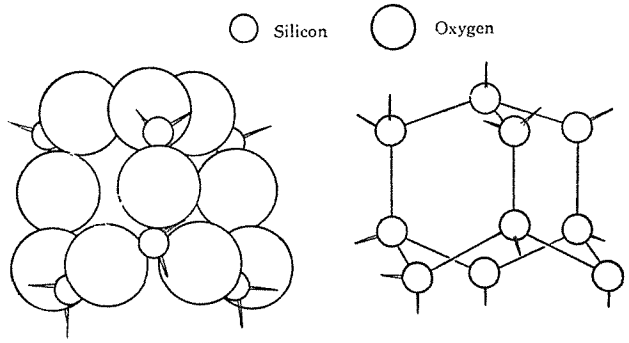
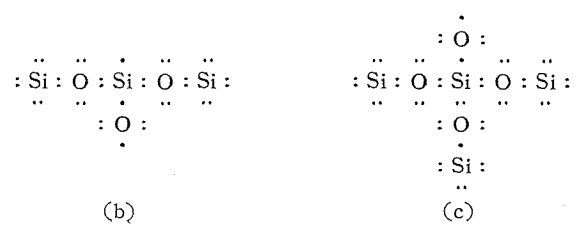


Fig. 1a. The structure unit of high cristobalite.

In Fig. 1a are shown the models of such a structure unit. Each Si has free bonds emerging from the atoms, on which some explanation would be necessary. Fig. 1b represents schematically the electron configuration of Si-O

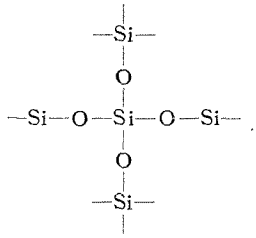


(b) (c)

Fig. 1b and c. The Schemes of binding Si and O to form a retwork.

chain indicating that there are two non-pairing electrons, one in Si-orbit and the other in O-orbit. In a continuous network they are bonded to O and Si, respectively, as shown in Fig. 1c.

As the matter of convenience the author is going to represent such free bonds by (O/2) as shown in Fig. 1d.



Fg. 1d. A schematical representation of the process of extending a chain by (O/2).

By this way the cristobalite structure unit may be formulated as

$$4\{[Si_6O_6](O/2)_{12}\} = Si_{24}O_{[24+48/2]} = 24SiO_2 \qquad (1)$$

From above it may be stated that a structure unit is an assembly of small number of atoms forming a solid structure, and having the stoichiometrical composition. It should be noted that there are many structure units corresponding to the same chemical composition, which however, may be classified into groups so that we may find out some regularities existing among them.

4. Formulation of Structure Units

As the first step we assume that the three-dimensional continuous network is composed of Si-O rings, and that the number of Si atoms in the rings are 4 to 8. Even under these limitations there are many ways of combining the rings into a solid structure which gives the chemical formula of SiO_2.

Solid models may be formed by bridging the rings with chains. High cristobalite structure unit, for example, is formed when three alternate corners of a hexagonal rings are bound together by a bundle of three chains $(Si—O—)_3$ which are linking to one Si-, i.e., $[(SiO)_3\ Si](O/2)_{10}$, in which (O/2)'s furnish (O/2) when the unit structure is extended.

This process may be formulated as

$$[Si_6O_6](O/2)_{12} + [(SiO)_3Si](O/2)_{10} \rightarrow [Si_{10}O_{[9+3]}](O/2)_{[22-6]} = 10\ SiO_2, \qquad (2)$$

in which $O_{[9+3]}$ and $(O/2)_{[22-6]}$ indicate that three new O's are formed at the points of bridging with the cost of six (O/2)'s.

As mentioned before, the tetrahedron so formed with 10 SiO_2 may be represented as

$$4\{[Si_6O_6](O/2)_{12}\} \rightarrow [Si_{[24-(2\times4+12/2)]}](O/2)_{[48-(4\times5+12)]}$$
$$= [Si_{10}O_{12}](O/2)_{16} = 10\ SiO_2. \qquad (2a)$$

Once we know the number of 4-8 rings of Si forming a solid structure and the number of its apices it is possible to compute the suffixes to Si, O, (O/2) without the help of a model. The calculation is carried out as follows:

If n be the number of apices, and m the total number of Si, then $m-3n$ will be the number of Si forming the edges, since 3 Si must unite to one at the corner when a solid structure is formed.

By this reason the total number of Si will be reduced from m to

$$m-\left(2n+\frac{m-3n}{2}\right),$$

because $2n$ at the corners, and the rest of Si at the edges are shared between two nearest neighbours.

In a ring the number of Si is equal to that of oxygen, and as in a solid structure the edges are common between two rings the total number, m, of O will be reduced to $m/2$.

At the apices 6(O/2) will be reduced to 1, and at the edges half of the $2(m-3n)$ (O/2) will disappear. The figures in the parenthesis suffixed to each letter give the examples of the above calculations.

It should be noted that there are many structure units belonging to a groups, whose number increases with the increasing Si in the group formula of Table 1. The number of the structure units belonging to the group $[Si_{10}O_{12}](O/2)_{16}$, for example, in which $n=4$ and $m=24$ is 8, even if we do not take into account the difference due to the relative position of the rings in the structure. That is to say there are 7 different structure units which may be regarded as being derived from high cristobalite $4\{[Si_6O_6](O/2)_{12}\}$, when we don't care the relative position of rings. They are the assembly of 4-8 rings having more or less deformed structures.

Furthermore, a family may include different groups each having different number of apices. $9SiO_2$, for example, represents $[Si_9O_{10}](O/2)_{16}$ and $[Si_9O_{11}](O/2)_{14}$, the former has 2 apices, while the latter has 4.

In Table 1 are listed the families, groups, and an example of structure unit belonging to each group. In this Table structure units are represented by the number of Si forming the rings, because there are as many O as Si and twice as many (O/2). Hereafer we shall use these abbreviated notations.

It will be seen that there are so many structure units representing the chemical composition SiO_2. This, however, does not mean that each structure

Table 1. Structure units of SiO_2 network.

Number of apex	Family	Group	Structure unit (an example)
2	$7SiO_2$	$[Si_7O_8](O/2)_{12}$	$2Si_5Si_6$
2	$8SiO_2$	$[Si_8O_9](O/2)_{14}$	$3Si_6$
2	$9SiO_2$	$[Si_9O_{10}](O/2)_{16}$	$2Si_7Si_6$
4	$10SiO_2$	$[Si_9O_{11}](O/2)_{14}$	$Si_4Si_5Si_6Si_7$
4	$10SiO_2$	$[Si_{10}O_{12}](O/2)_{16}$	$4Si_6$
4	$11SiO_2$	$[Si_{11}O_{13}](O/2)_{18}$	$3Si_6Si_8$
6	$12SiO_2$	$[Si_{12}O_{15}](O/2)_{18}$	$5Si_6$*
20	$20SiO_2$	$[Si_{20}O_{30}](O/2)_{20}$	$12Si_5$**

* High Tridymite, ** Tilton's vitron.

unit has the equal probability of existence. Some of them would predominate number, while others would be comparatively few. In fact Tilton has advanced the "non crystal ionic model" which is built of pentagonal rings forming a dodecahedral cage, *a vitron*. This structure unit is

$$12\{[Si_5O_5](O/2)_{10}\}=[Si_{20}O_{30}](O/2)_{20}=20\,SiO_2 \qquad (3)$$

He was able to account for some characteristic properties of vitreous silica by his vitron theory.

On the other hand Oberlies and Diezel have the opinion that the structure of vitreous silica has a striking resemblance to that of high cristobalite. According to this view vitreous silica may be represented as

$$[Si_{10}O_{12}](O/2)_{16}, \qquad (4)$$

while

$$4\{[Si_6O_6]\}(O/2)_{12}$$

represents that of high cristobalite.

5. Hole and Hole Volume

It is generally accepted that there are holes of various sizes in silica network, and the object of the present article is to evaluate the average size of these hole volumes which vary with the structure units.

Obviously, a hole volume in glass structure is not an isolated volume in continuous medium, but a void space surrounded by a number of rings which in itself has holes. Strictly speaking it is, therefore, impossible to demarcate the exact volume. Moreover, as stated before, there are so many structure units each being able to form at least a part of continuous network. Therefore, let us try to estimate the order of magnitude of the average hole volumes for some typical structure units.

The hole volume per atom of oxygen. Volume of Si^{4+} is negligibly small as compared with that of oxygen so that the volume of vitreous silica may be regarded as being composed of the volume of O^{2-} and that of the holes. Therefore the hole volume per formula weight of SiO_2, V_{h0} may be estimated by

$$V_{h0}=\frac{60}{d}-2mV_0 \qquad (5)$$

where m is the number of Si atoms, i.e. 6.02×10^{23}, V_0 the volume of oxygen atom, 10.3 A^3 whose radius is 1.35 Å, and d is the density of vitreous silica, 2.203.

This equation gives the result

$$V_{h0}=14.8\text{ cc}$$

which gives 11.5 $Å^3$ as the hole volume per atom of oxygen.

There are two ways leading to the estimation of an average value of the hole volume of single structure units of a family, m SiO_2, or of a group $[Si_aO_b](O/2)_c$.

b. Estimation of hole volume from silicon balance. An approach to the estimation of the average hole volume of a family of structure units, m SiO_2, is to resolve the continuous network into structure units, and then evaluate the

number of units N_h contained in one formula weight of SiO_2. As the total hole volume of vitreous silica is known to be 14.8 cc the quotient

$$q=\frac{14.8}{N_h}$$

will give the average hole volume of the structure units.

Although the study with model is the best way for obtaining the most clear picture covering all possible cases the following argument might be of some help to get a rough idea :

Let us consider a chain

$$(O_2O_3O_4)SiO_1Si'(O_5O_6O_7),$$

in which the six oxygens in the parentheses are making the tetrahedral angle with the bond Si-O-Si', and try to find out the number of structure unit with which Si is shared. In this paragraph the subscript of oxygen and prime of silicon mean the different oxygens and silicon respectively.

There are three structure units around Si whose edges are

$$(O_2O_3),\ (O_3O_4),\ (O_4O_2).$$

Furthermore, Si O_1 Si' becomes a part of chains bridging the rings to form new solid structures, and Si' again has three oxygens which form the edges

$$(O_5O_6),\ (O_6O_7),\ (O_7O_5),$$

which means that Si is shared with other three units. In other words if the number of Si atoms were increased six times as many the whole network may be resolved into structure units. Hence the total number of Si necessary for this process is

$$6\times6.02\times10^{23},$$

which gives the number of structure units N_h by dividing with m. In Table 2 is given the number of structure units, N_h, as well as the hole volumes.

Table 2. Number of structure units in a forumla weight of vitreous silica, and their hole volume.

Family	Number of structure units ($\times10^{23}$)	Average hole volume in A^3
$7SiO_2$	5.2	28.7
$8SiO_2$	4.5	32.8
$9SiO_2$	4.0	37.0
$10SiO_2$	3.6	41.0
$11SiO_2$	3.3	44.8
$12SiO_2$	3.0	49.4

From the figures is will be observed that the hole volume increases with the increasing number of Si atoms in the structure.

Moreover, it should be noted that these are the average values of the units having the same number of Si atoms, but different hole volumes.

c. Estimation of hole volume from the number of oxygen. Each oxygen in vitreous silica is assigned the hole volume of 11.5 A^3. In the same fashion as before it would easily be understood that O_1 in the chain gives in preceding paragraph takes a part of three structure units irrespective of the relative position of O_2-O_7. In other words every oxygen in the network is shared by three units. Hence we may evaluate the average hole volume of a group from the relation

$$\frac{11.5\times b}{3}\ \text{Å}^3.$$

In Table 3 are given the results of the calculstions, together with the difference between the hole volumes obtained by the methods (b) and (c).

Table 3.

Group	Hole volume in Å^3	Difference of Vh_0 estimated by the methods (1) and (2) in Å
$[Si_7O_8](O/2)_{12}$	30.6	1.9
$[Si_8O_9](O/2)_{12}$	34.6	1.8
$[Si_9O_{11}](O/2)_{14}$	42.2	2.2
$[Si_{10}O_{12}](O/2)_{16}$	46.0	5.0
$[Si_{11}O_{13}](O/2)_{18}$	50.0	5.2
$[Si_{12}O_{15}](O/2)_{18}$	56.3	6.9
$[Si_{20}O_{30}](O/2)_{20}$	115	

It will be seen that the method (b) and (c) give more or less different results, and the difference becomes larger with increasing hole volumes. Probably these differences are the outcome of the accumulation of small amount of errors accompanied with the rough estimation of the values.

9. Some Physical Characteristics of Vitreous Silica

Let us try to explain some physical characteristics of vitreous silica in terms of the structure unit.

a. The density. The average value of the density, of structure units may be represented by

$$\rho=\frac{6\times 60}{27\times 10^{24}}\ \text{g/Å}^3. \qquad (6)$$

In the equation the molecular volume, 27 cc/mole, of silica was used in place of 14.8 cc, because in this case the volume of oxygen atoms should have been taken into account.

Also, the evaluation of the density ρ' of a group $[Si_aO_b]\ (O/2)_c$, leads to the same value, $\rho'=\rho$, if we remember the relation

$$b+\frac{c}{2}c=2a,$$

and assign to c the half of the oxygen volume.

At first sight it will appear unproved that the density of a single structure

unit is six times as large as the ordinary value, 2.203. This, however, comes from the fact that each m Si and 2m O in the structure unit is shared, respectively, by six and three nearest neighbours. This means that the continuous network may be assembled with 1/6 Si and 1/3 O of the total numbers of Si and O with which the structure units are built.

It should be noted that from the equation (6), that is to say, there is a set of structure units which gives always a constant density value even if the units were mixed up with any arbitrary proportions. This comes from the fact that the degree of packing of Si and O at the surface of structure unit increases in exact proportion to the increase of its volume,

$$\frac{m_1}{(V_1)^{2/3}}=\frac{m_2}{(V_2)^{2/3}}=\cdots\cdots=k, \qquad (7)$$

in which m_1, m_2 ····· are the mass of structure units, m_1 SiO_2 etc, $(V_1)^{2/3}$, $(V_2)^{2/3}$·····their surface area, and k the surface density.

Obviously, this is the natural result of our method of evaluating the density of a structure unit, because we have started from a single density value of silica. The argument, however, would suggest that the *density dose not reflect the inhomogeneity of structure units.*

All three crystalline silica, quartz, tridymite, and cristobalite show high-low inversions which conventionally are interpreted as coming from the change of bond angles and distances caused by the rotation of the Si-O chain. Although a perfectly stabilized glass gives a single definite density value irrespective of its thermal history this may be explained in two ways, namely, (1) by assuming only one set of the units, having only one, say, k value which are in internal equilibrium under a given environment, or alternately, (2) by assuming the equilibrium among more than two sets of units existing in such a proportion that gives the same density value as before.

If we venture to assume that the first set of units, say,

$$\frac{7SiO_2}{(V_7)^{2/3}}=\frac{8SiO_8}{(V_8)^{2/3}}=\cdots\cdots=k_1,$$

predominates in the network being in internal equilibrium at a temperature interval t_1-t_2, and in another interval t_2-t_3 the second set, say,

$$\frac{7SiO_2}{(V_7)^{2/3}}=\frac{8SiO_2}{(V_8)^{2/3}}=\cdots\cdots=k_2$$

represents the family of the structure units which are the building stones of the equilibrium network, we may expect the transition with volume change at t_2 as in the case of crystalline silica. There is, however, a difference between the transition of glass and crystal which is built by piling up a single unit cell. A "high-low" inversion occurs practically instantaneously and is reversible, but the number of allowable structure unit and the versatility of the allowable arrangements to form a glass network would bring out such an irregularity which prohibits the simultaneous change of configuration throughout the mass. As a result hysteresis would be observed in the measurement of expansion and

contraction of glass.

The above statement is nothing but a version of the idea advanced by Fajans and Barber[6] who interpreted successfully the anomalies in the expansion of vitreous silica by assuming the equilibrium between two kinds of atomic group, and also of the other similar conceptions which admit the existence of some atomic groups in glass structure. The author would like to extend these theories by assuming the equilibrium between the families of the structure units each having different surface densities. As the matter of course the whole structure is a random network, but it contains the elements of the families which lead to different density values. It might be admitted that this conception of the structural inhomogeneity acts as a bridge between the random network theory and those claiming the existence of some atomic groups in glass structure.

b. Diffusion of gases. It is well known that some gases such as hydrogen and helium pass through vitreous silica, while the permeability to the other rare gases having larger diameter such as argon, and nitrogen is extremely small. Norton[7], for example, has estimated the rate of diffusion of neon (atom diameter 2.4A) and argon (3.2A) with a result that the rate of diffusion of the former is 10^5 times as large as that of the latter. An illustration of this property was given by taking into account of the hole diameter of the rings, Indeed argon can not pass through a Si_6-ring while it can pass freely a Si_7-ring as

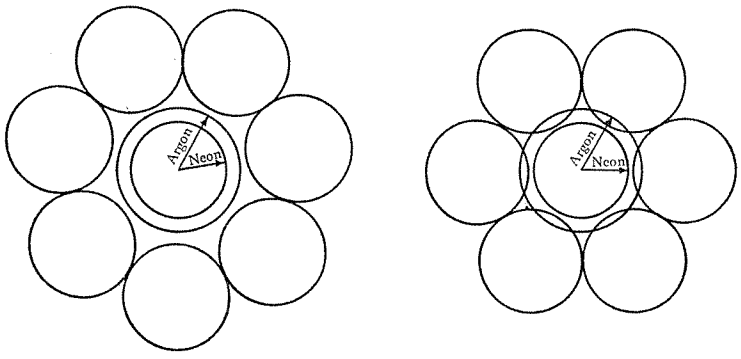


Fig. 2. Hole diameter of Si_6- and Si_7-rings and the diameter of Ne and A atoms.

Table 4. Structure units belonging to the group $[Si_{10}O_{12}]$ $(O/2)_{16}$

	Structure unit	Remark
I	$4Si_6$	High cristobalite
II	$Si_62Si_6Si_7$ $2Si_5Si_6Si_8$ $Si_42Si_6Si_8$	Structures containing one 7 or 8 rings
III	$Si_4Si_62Si_7$ $Si_4Si_5Si_7Si_8$ $2Si_52Si_7$ $2Si_42Si_8$	Structures containing more than one 7. 8 rings.

Fig. 2 shows the relation.

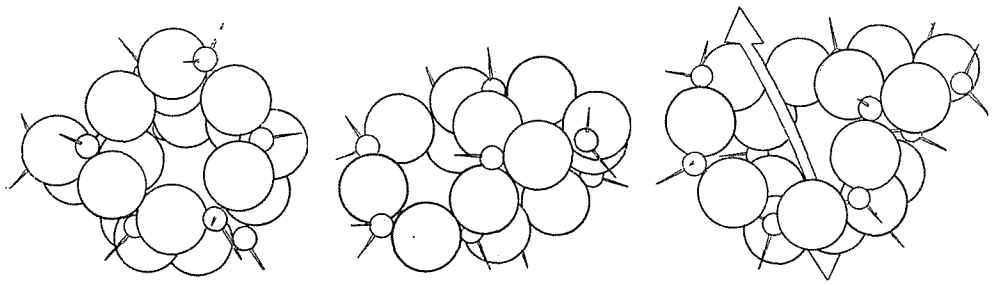
In order to discuss the matter in some detail let us follow after the process of building the network from structure units taking the group $[Si_{10}O_{12}]$ $(O/2)_{16}$ as the simplest example of those structure units which contain more than one Si_7 or Si_8-rings. In Table 4 are listed the units of this groups classified according to the number of the larger rings Si_7 and Si_8

From the Table let us pick up three units containing one Si_7-, one Si_8- and two Si_7-rings and try to form the network formed of two units, namly,

$$\begin{array}{ll} 2Si_5 2Si_6 Si_7 & 2Si_5 2Si_6 Si_7 2Si_6 2Si_5 \\ 2Si_4 2Si_6 Si_8 & 2Si_4 2Si_6 Si_8 2Si_6 2Si_4 \\ 2Si_4 Si_6 2Si_7 & 2Si_4 Si_6 Si_7 Si_7 Si_7 Si_6 Si_4 \end{array} \qquad (7)$$

The model of the solid structures are reproduced in Fig. 3 a-c.

Now the formulae in (7) are telling that networks two structure units may be formed by the union of any two rings. This is possible, because we have resolved the network by counting the rings twice. The autuel process is not so simple as indicated, since we should have to bridge the rings by chains so that some members of the ring are shared by another one as shown in Fig. 3a and b.



(a) (b) (c)

Fig. 3. The solid models containing Si_7- and Si_8-rings.

At any rate there is one rule which states that there remains only one Si_7- or Si_8- ring as long as each original unit contains one such large ring. In other words, in the network formed from two such units the large ring is covered by smaller ones through which argon can not pass. Even if a glass network contains the rings which has the holes large enough to allow the free pass of the rare gases of larger atom diameter the diffusion through the whole mass does not occur as long as the larger rings are covered by the smaller ones.

The situation becmes quite different when the structure unit contains more than two larger rings. The last formula in (7) shows that there are two more Si_7- rings next to Si_7, which suggests that three successive Si-rings remain in network providing the passage way for larger gas atoms. In Fig. 3c the array of Si_7-rings is indicated by an arrow.

Bridging the Si-rings by $\overset{O}{O}\!>\!Si\!-\!O\!-\!Si\!-\!O$ or $O\!-\!Si\!-\overset{O}{O}\!>\!Si\!-\!O\!-\!Si\!-\!O$ it is possible to continue the costruction of the network in the manner :

$$\begin{array}{lll} Si_4Si_62Si_7 & Si_4Si_62Si_7 & 2Si_42Si_66Si_7 \\ 2Si_42Si_63Si_7 & Si_4Si_62Si_7 & 3Si_43Si_64Si_7 \\ 3Si_43Si_64Si_7 & Si_4Si_62Si_7 & 4Si_44Si_65Si_7 \end{array} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (8)$$

A model of $4Si_44Si_65Si_7$ is shown in Fig. 4.

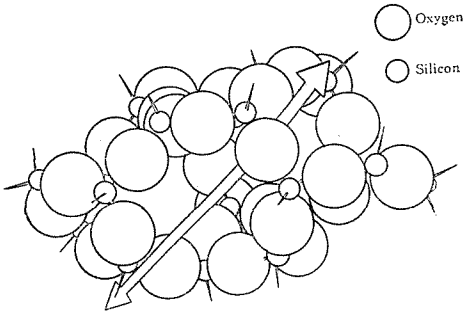


Fig. 4. A model of $4Si_44Si_65Si_7$

It will be seen that there still remains a path framed in Si_7-ring in the network. The characteristic property of vitreous silica to the diffusion of rare gases suggests that in the network the structure units containing more than one Si_7- or Si_8-rings are completely enclosed by those containing less than single member of larger rings.

c. Melting and devitrification. Silica has rather high melting point among ordinary glass forming substances. In fact it melts at 1720°C to a very viscous liquid, and it turns always into a glass and not into a crystal as long as the molten mass is cooled down with an ordinary rate. By prolonged heating at the temperature as low as about 1000°C it begins to devitrify. The devitrification does not occur simultaneously within the whole mass, but, as it is well known, the crystallization starts locally from a number of centers.

It seems that these characteristic properties afford a very convenient clue for studying the structure of vitreous silica, because they provide a gate way connecting crystalline silica with vitreous one. The structure of the former is well established, while that of the latter is indeterminable being blocked by the idea of the randomness of the network.

Let us try to discuss the matter in the following order :

i. Melting of silica. The fact that high cristobalite melts at very high temperature suggests that the bond strength of Si-O is large enough to hold the the structure firmly against the strong thermal agitation. It is, therefore, natural to suppose that the structure of high cristobalite is retained in considerable degree just as water is well know to have quartz like structure at lower temperature. This assumption makes us suppose that the flow units in molten silica should be large, and this is supported by its high viscosity even at very high temperatures.

ii. Formation of vitreous silica. Molten silica is always cooled down to glass but not to crystal. This suggests that the probability of forming a cristobalite lattice would be very small compared with that of forming a random

network. In fact there are a number of the structure units leading to formation of the deformed, random network, while there is the only one, $4Si_6$, which can form the cristobalite lattice.

Probably it would be better to speculate the process of forming the glass network in some detail. In the first place the auther ventures to assume that even in molten state the cristobalite lattice has not been broken up entirely to separate atoms, but there remains at least the shadow of the former structure, so that the melt is composed of chains and rings which, probably, are partly linking. They would join and disjoin each other, or change the point of linking all the time. This means there remain some kinds of structure units although they might be imperfet and would be changing from one to another at every moment.

Cristobalite has the structure in which three alternate corners of a hexagonal ring, say, (1, 3, 5) are bound together by Si $[SiO_{-(0/2)_3}$. Now if by chance the binding occurs at (1, 2, 6) during the formation of a network the structure unit $Si_52Si_6Si_7$ would be obtained, and by binding at corners (1, 2, 6) the structure unit $2Si_5Si_6Si_8$ would be formed. Both are so deformed that It is not possible to build a regular crystalline pattern. Furthermore the strain which has necessarily been brought with process of building a network from deformed units would accumulate more and more during the course of extending the structure to such a degree that it prohibits the further extension without using other units. Consequently, a glass network should be regarded as being an assembly of many structure units leading to the structural inhomogeneity of the network, which, however, does not reflect on such a bulk property as density.

iii. The devitrification. Vitereous silica begins to devitrify by prolonged heating at the temperature near Tg (1200°C), and the primary crystal that appears from glassy phase at any temperature is always known to be high cristobalite. The process of forming cristobalite unit from others, for example,

$$Si_4Si_62Si_7 \rightarrow 4Si_6$$

may be imagined as being carried out through a number of steps of changing the orientation of atoms successively until we obtain the final structure, $4Si_6$. Such number of steps would vary according to the initial siructure unit, and in Table 5 are listed the number of steps necessary for the transformation form glass to cristobalite unit.

Now, it will easily be undersood that there will be existing a number of

Table 5 Number of steps in the rearrangements to form $4Si_6$ from other members of the groups $[Si_{10}0_{12}](0/2)_{16}$

$2Si_52Si_6Si_7$	1
$2Si_5Si_66Si_8$	2
$2Si_52Si_7$	3
$Si_4Si_62Si_7$	4
$2Si_42Si_8$	4

potential wells of different depths throughout the network as long as there are many structure units in it. And from points of higher energy the devitrification will start.

SUMMARY

Crystal is always more homogeneous than glass. In other words, glassy state is characterized by the structural inhomogeneity which states that glass network is an assembly of different structure units.

For example $[Si_{10}O_{12}](O/2)_{16}$ represents an impotant part of the framework of vitreous silica, while $4[Si_6O_6](O/2)_{12}$ is the elemental building stone of high cristobalite.

At first glance the above statement looks like to be another version of the random network. However, the introduction of the conception of structure unit allows us to picture the nature of the network from which we may draw out some interesting conclusions.

Some of them are touched in this text, namely:

(1) The bulk property such as density does not reflect the structural difference of randon network as long as it is built of the structure units having the same surface density. The larger the hole volume of an unit the larger will be its surface density.

(2) The rate of diffusion of rare gases having different atomic radii throuh silica network may be interpreted by the conception of structure units even if we admit the existence of the rings being enough to give the opening which by itself provides the passage way for the gases of larger diameter.

It is interesting to know that some units leave the passage for larger molecules in any type of their assembly, while in others such an opening will be closed by the process of piling them up. In a glass network, therfore, the former should be enclosed by the latter.

(3) The fact that molten silica solidifies always into glass may be understood by taking into account of the versatility of the possibilities of composing a glass network from various kinds of structure units while the assembly of the high cristobalite lattice has the only one possibility of piling up the single units, $4Si_6$. Furthermore, the devitrification which starts from comparatively few points may be explained by considering the number of steps necessary for the rearrangement from a deformed to the regular cristobalite lattice.

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